472 *J. Phys. Chem. A* **2000,** *104,* 472−475

Microscopic Dynamics of Deterministic Chemical Chaos

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Received: July 13, 1999

The master equation of a chemical model for the Lorenz equations was examined by ensemble simulations in this paper. It was found that, due to the fast separation of nearby simulation runs, the representative points in the ensemble which initially assembled densely in the concentration phase space fell apart and extended to distribute on the overall chaotic attractor. Results revealed that intrinsic fluctuations in systems of deterministic chemical chaos are very large and the ensemble-averaged values of concentration are therefore meaningless. Nevertheless, the structure and dynamics of individual simulation runs, which are numerical realizations of the underlying jump Markov process, are in good coincidence with the deterministic chaotic attractor.

I. Introduction

Noise can play an important role in the development of nonequilibrium phenomena such as chemical oscillations and chaos, chemical waves, and patterns. For instance, in nonequilibrium transition processes the effect of noise is often crucial.[1] Positive and constructive effects of noise have also been found in the recent year's studies of stochastic resonance.[2] For intrinsic noise in systems of deterministic chemical chaos, the situation is somewhat intriguing. Chaotic dynamics is characterized by its sensitivity to initial conditions and is susceptible to external disturbances. One expects that intrinsic noise arising from the molecular nature of the system could similarly also have pronounced effects on chaotic dynamics. Questions such as would chaotic dynamics amplify internal noises and destroy the macroscopic description, and what the deterministic chemical chaos would become in the picture of a microscopic description beyond the phenomenological kinetics, are of much interest. The situation is somewhat similar to that of quantum chaos where people ask what classical chaos in Hamilton systems would become or manifest itself in the picture of quantum mechanics where one has to give up the concept of classical trajectories and to use probabilistic wave functions. As is well-known, chaos is originally defined for deterministic dynamical systems and is often termed as "deterministic" chaos. Strictly, chaos may have no meaning in a stochastic system. In a microscopic or mesoscopic description, the counterpart or analogue of a deterministic chaotic trajectory would also be interesting.

In previous studies concerning the problem,[3−8] approaches used include Fokker−Plank equations,[3] reactive lattice-gas automaton,[4] and particle simulation method.[5] In addition, several authors have applied the master equation approach,[6−8] most of which have been mainly concerned with comparison between single simulation runs and phenomenological chaotic attractors. Conclusions arrived at in these studies were sometime inconsistent.[9] In this paper, we study the master equation for the chemical Lorenz system, which is a chemical model for the Lorenz equations, by means of ensemble stochastic simulations. Our calculations provide rather direct information on the underlying microscopic dynamics and therefore can be used to discuss the questions raised above. There have been previous master equation studies of the chemical Lorenz system also by means of ensemble simulations.[8] The size of the system used in these studies was comparatively small and because of this would have introduced intensive extra intrinsic fluctuations. In this paper, particular attention has been paid to diminish the internal fluctuations due to finite system size. We reexamined the master equation with large system size for the model. Results presented here reveal a clear mesoscopic picture of deterministic chemical chaos. In the rest of the paper, the model and the approach employed are introduced in section II; section III reports the main results of our calculations. A brief discussion is included in section IV.

II. Master Equation and Method

The famous Lorenz system can be interpreted chemically.[10,11] By applying a nonlinear transformation, the original Lorenz equations,[12] the right side of which consists of polynomials, can be translated into a new form that allows only nonnegative state variables but preserves the phase space qualitative features of the original system.[10] The new set of equations is stills of polynomial form and therefore can be readily interpreted chemically on the base of mass action law as follows:

$$
\begin{gathered}
X + Y + Z \xrightarrow{k_1} X + 2Z, \quad 2X \xrightarrow{k_6} P_2, \quad Y \xrightarrow{k_{11}} P_6 \\
A_1 + X + Y \xrightarrow{k_2} 2X + Y, \quad 2Y \xrightarrow{k_7} P_3, \quad A_4 + Y \xrightarrow{k_{12}} 2Y \\
A_2 + X + Y \xrightarrow{k_3} X + 2Y, \quad 2Z \xrightarrow{k_8} P_4, \quad A_5 + Z \xrightarrow{k_{13}} 2Z \\
X + Z \xrightarrow{k_4} X + P_1, \quad A_3 + X \xrightarrow{k_9} 2X \\
Y + Z \xrightarrow{k_5} 2Y, \quad X \xrightarrow{k_{10}} P_5
\end{gathered}
\tag{1}
$$

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10.1021/jp9923623 CCC: $19.00

In the above reaction network, parameters k_i ($i = 1, 2, ..., 13$) over the arrows are rate constants. Concentrations of species A_i ($i = 1, 2, 5$) and P_i ($i = 1, 2, ..., 6$) are assumed to be constant in order to constrain the system far out of equilibrium. Given a well-stirred reactor and ideal mixture, the phenomenological rate equations of mass action law for the above reaction system read

$$
\begin{aligned}
\mathrm{d}x/\mathrm{d}t &= k_2xy - 2k_6x^2 + k_9x - k_{10}x \\
\mathrm{d}y/\mathrm{d}t &= -k_1xyz + k_3xy + k_5yz - 2k_7y^2 - k_{11}y + k_{12}y \\
\mathrm{d}z/\mathrm{d}t &= k_1xyz - k_4xz - k_5yz - 2k_8z^2 + k_{13}z
\end{aligned}
\qquad (2)
$$

where x, y, and z are concentrations of species X, Y, and Z, respectively, and concentrations of A_i ($i = 1, 2, 5$) have been incorporated into the rate constants k_2, k_3, k_9, k_{12}, and k_{13}. Equation 2 can exhibit various nonlinear behaviors qualitatively similar to the original Lorenz system.

Under the same conditions for kinetics (2), and provided that elastic processes are much more probable than reactive events so that memory loss of history is guaranteed, the above system can be well considered as discrete Markov jumps in the population space of the X, Y, and Z species. The time evolution of the reaction systems is thus governed by the chemical master equation. Ω in the above equation is a parameter denoting the size of the system, and the thermodynamic limit is fulfilled when Ω goes to infinity. Parameters k_i ($i = 1, 2, ..., 13$) are reaction rate constants as in eq 2. The chemical master equation, whose rigorous microphysical basis and validity have been proved for well-stirred gas-phase chemical systems in thermal equilibrium,[13] describes the reaction system (1) at a more realistic mesoscopic level and therefore provides a good foundation for studying the corresponding microscopic dynamics of the phenomenological kinetics in regimes of chaos.

$$
\begin{aligned}
\frac{\partial}{\partial t}P(X,Y,Z,t) = {}& \frac{k_1}{\Omega^2}[X(Y+1)(Z-1)P(X,Y+1,Z-1,t) - \\
& XYZP(X,Y,Z,t)] + \frac{k_2}{\Omega}[(X-1)YP(X-1,Y,Z,t) - \\
& XYP(X,Y,Z,t)] + k_3[X(Y-1)P(X,Y-1,Z,t) - \\
& XYP(X,Y,Z,t)] + k_4[X(Z+1)P(X,Y,Z+1,t) - \\
& XZP(X,Y,Z,t)] + \frac{k_5}{\Omega}[(Y-1)(Z+1)P(X,Y-1,Z+1,t) - \\
& YZP(X,Y,Z,t)] + \frac{k_6}{\Omega}[(X+2)(X+1)P(X+2,Y,Z,t) - \\
& X(X-1)P(X,Y,Z,t)] + \frac{k_7}{\Omega}[(Y+2)(Y+1)P(X,Y+2,Z,t) - \\
& Y(Y-1)P(X,Y,Z,t)] + \frac{k_8}{\Omega}[(Z+2)(Z+1)P(X,Y,Z+2,t) - \\
& Z(Z-1)P(X,Y,Z,t)] + k_9[(X-1)P(X-1,Y,Z,t) - \\
& XP(X,Y,Z,t)] + k_{10}[(X+1)P(X+1,Y,Z,t) - XP(X,Y,Z,t)] + \\
& k_{11}[(Y+1)P(X,Y+1,Z,t) - YP(X,Y,Z,t)] + \\
& k_{12}[(Y-1)P(X,Y-1,Z,t) - YP(X,Y,Z,t)] + \\
& k_{13}[(Z-1)P(X,Y,Z-1,t) - ZP(X,Y,Z,t)]
\end{aligned}
\qquad (3)
$$

The master equation (eq 3) is rather complex and is not amenable to analytic resolution. We here refer to the Monte Carlo simulation algorithm due to Gillespie.[14] This approach is a scheme of carrying out numerical realizations on a computer of the underlying jump Markov process on which the master equation is based. (Refer to ref 14 for the details of Gillespie's algorithm.) Starting from an initial condition of populations for X, Y, and Z species, the implementation of the algorithm produces a stochastic trajectory, i.e., a single realization of the Markov process. A big collection of such simulation runs is expected to be representative of the time evolution of the chemical master equation, and the statistics on it should be equivalent to the properties from the probability $P(X,Y,Z,t)$ in the master equation. We prepared a population of initial conditions when carrying out stochastic simulations of eq 3. Statistical properties were calculated when the ensemble evolved forward in time. Special attention was paid to the scale factor Ω measuring the system size. For small values of Ω, the internal fluctuations are doomed to be large. To diminish the contribution to the intrinsic noise due to limited system size, we used the value 30 000 for Ω. Using this value, we find that the system size effect becomes trivial, at the expense of tremendously more computer time. In our calculations, the population of species X, Y, and Z species typically amount to over 6 000 000.

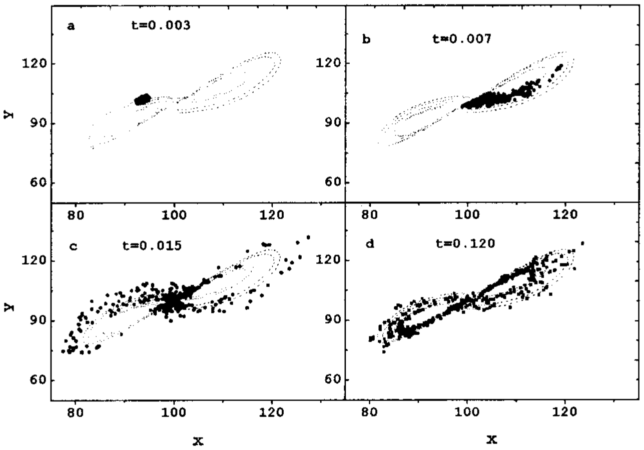

Figure 1. Phase space distributions (projected onto $x-y$ plane) of a population of 400 representative points at four different time showing dispersion. The background trajectory (dashed line) in the panels is a fraction of a deterministic chaotic trajectory under the same reaction rates. Parameters: $k_1 = 1$, $k_2 = 10$, $k_3 = 29$, $k_4 = 100$, $k_5 = 100$, $k_6 = 5$, $k_7 = 0.5$, $k_8 = 1.3333$, $k_9 = 1000.0$, $k_{10} = 1000$, $k_{11} = 2900$, $k_{12} = 100$, $k_{13} = 10\,002.6667$, $\Omega = 30\,000$.

III. Results

The phenomenological kinetics (eq 2) supports nonlinear behavior such as steady states, limit cycles, and chaos under appropriate parameter values. In the chaotic regime, we inspected the time evolution behavior of a population of 400 representative points of the system that initially assembled densely in a very small volume of the population phase space. All representative points in the ensemble were simulated simultaneously and thus each point evolved into a stochastic orbit representing an individual realization of the jump Markov process in the phase space. Figure 1 shows the distribution of the representative points in the concentration phase space at four successive points of time. In the demonstration, the populations of X, Y, and Z species have been converted into concentrations by dividing the particle numbers by the system size factor Ω. From Figure 1, it is readily seen that the representative points that were initially dense in the phase space fell apart when the time proceeded and were wildly scattered in the phase space after a certain period of time. This dispersion behavior implied a greatly expanded probability distribution of $P(X,Y,Z,t)$ in the master equation. The background trajectory

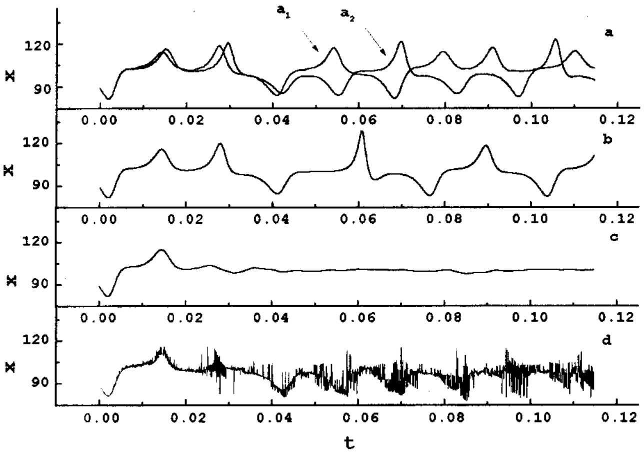

Figure 2. Time evolution of the concentration of the X species: two typical simulation runs with very close initial conditions (a) showing rapid separation, a fractional deterministic trajectory (b), ensemble-averaged *x* concentration from simulation (c), and the most probable value (d). Parameters are the same as in Figure 1.

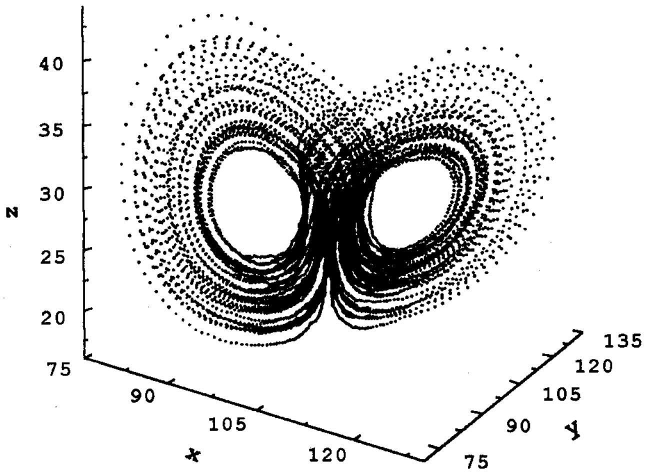

Figure 3. Typical "chaotic attractor" of simulation, i.e., a single stochastic simulation run, taken from the ensemble. One can hardly discern any difference from the deterministic chaotic attractor produced by the rate equations.

in the panels of Figure 1 is a fraction of a chaotic trajectory produced by the deterministic rate equations. One sees that, although the representative points were finally distributed great diffusely, they were mostly restricted on the deterministic chaotic orbit.

The dispersion behavior of the representative points in the ensemble is obviously the direct consequence of fast separation of nearby stochastic simulation runs. Figure 2a shows this separation behavior of two randomly selected stochastic trajectories from the ensemble. In addition, this separation of nearby simulation orbits indicates very large intrinsic fluctuations. Since the representative points in the ensemble have been wildly dispersed and distributed on the overall deterministic chaotic attractor, the standard deviations of concentrations become rather large, and the averaged values of concentrations are therefore meaningless. Panel c in Figure 2 is the time evolution of the ensemble mean concentration for the X species. One sees that it cannot be a chaotic orbit. Rather, it resorted to a definite level after a certain period of time when a full dispersion is reached and deviated with small amplitude. Figure 2d shows the most probable value for the X species. For comparison, a fraction of a deterministic chaotic orbit is depicted in Figure 2b.

Although the averaged values of concentrations are meaningless, each simulation run in the ensemble is very similar to the deterministic chaotic attractor. As previously observed by other authors,[4−6] the phase space density of a simulation run closely resembles that of the chaotic attractor. Figure 3 depicts such an orbit from the simulated ensemble. Its phase space structure is in close accordance with its deterministic counterpart. Figure 4a shows the Poincaré surface sections of the simulated orbit in Figure 3 (open circles) and the deterministic chaotic attractor produced by eq 2 (dark dots). The two maps coincide and both show one-dimensional curves that are characteristic for dissipative chaotic systems. The good agreement of the 1D maps shown in Figure 4b constructed from the Poincaré surface sections prove even further the resemblance between the dynamics of the simulated orbit and deterministic chaotic attractor.

IV. Discussion

We have analyzed the master equation for the chemical Lorenz model by means of ensemble stochastic simulations. It was found that due to the separation of nearby stochastic trajectories, the representative points in the ensemble expanded to distribute on the overall deterministic chaotic attractor. The result revealed very large intrinsic fluctuations in systems of deterministic chemical chaos that made the averaged values of concentration meaningless. While the evolution path formed by the ensemble-averaged values is no longer chaos, individual simulation orbits preserved mostly the structure and dynamics of the deterministic chaotic attractor, as have also been found previously in the Williamowski−Rössler model.[4,5]

This microscopic picture of deterministic chemical chaos is much similar to its macroscopic counterpart when one prepares a large set of initial conditions that densely assemble in the phase space for the deterministic rate equations and examines their time evolution. Because of the sensitivity to initial conditions of chaos, one finds that the points also extend in the particle phase space. After a sufficiently long time when a full dispersion is reached, the representative points also tend to distribute on the overall strange and chaotic attractor. The position of a deterministic chaotic trajectory in the macroscopic description is quite analogous to that of an individual stochastic simulation run which is a single run realization of the underlying Markov process. In some sense, a deterministic chaotic orbit might be also "stochastic" because its numerical production from the macroscopic equations mostly depend on the mean by which it is generated, such as the specific numerical integration algorithm and the roundoff errors of the computer. At this point, a probabilistic description of deterministic chaos is more desirable. In a word, the ensemble pictures of macroscopic and microscopic dynamics are roughly comparable.

The validity of phenomenological equations in the chaotic regime was at one time a disputed topic.[9] Conclusions arrived at in previous studies were sometimes inconsistent. Specifically, approximate Fokker−Plank equation analyses[3] showed that when the macroscopic equations exhibit chaos, intrinsic fluctuations grew up very fast to macroscopic size and therefore destroyed the macroscopic description. They concluded that the macrovariable equations were unstable and cannot be justified from an underlying microscopic description. The group in Brussels[5,6] carried out stochastic simulations of the chemical master equation for models of chemical chaos and showed that "strange attractors" formed by individual simulation runs preserved the principal features of deterministic chaotic attractor. It was concluded that the macroscopic equations continued to describe the behavior of the most probable values, rather than

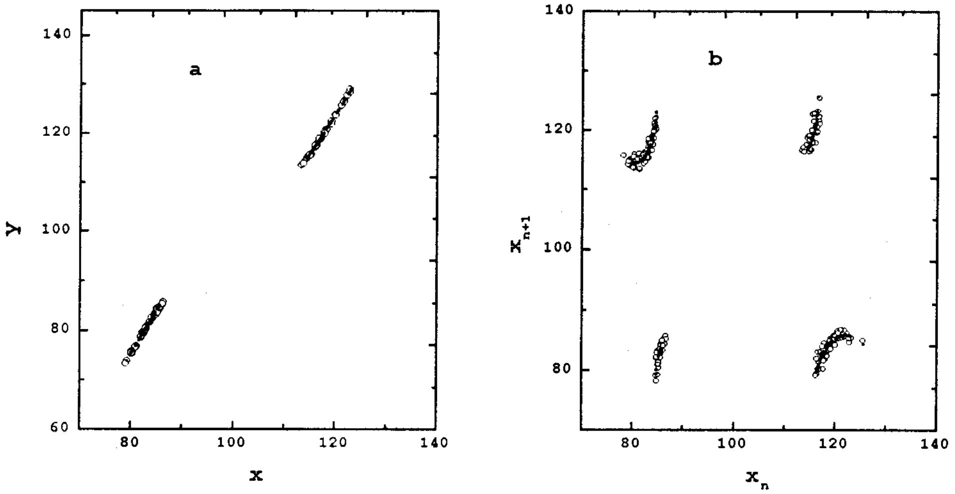

Figure 4. (a) Poincaré surface sections constructed from the simulation run in Figure 3 and the deterministic chaotic attractor (not shown) by plane $z = 30$; (b) 1D maps constructed from the Poincaré maps in (a). Simulation results (open circles) and deterministic results (dark dots) are in close accordance.

the mean value, of the variables and generate the system's chaotic attractor; therefore, the validity of the macroscopic equations was fully kept. Compared to previous simulation studies,[4-7] our ensemble simulations of the master equation presented a more complete picture of microscopic dynamics for deterministic chaos. We observed equally that individual simulation runs share consistent phase space structures with deterministic chaos, but it was also found that nearby simulation paths separate as time proceeds. The time evolution picture of the representative points of the ensemble in the phase space revealed that neither the ensemble mean nor the most probable value is representative of the system because of the greatly expanded distribution of the points of the ensemble which have explored the whole chaotic attractor. At this point, the system denies any macroscopic description. In this sense, the macroscopic equations lose theirsignificance and are invalid. While a microscopic description or at least a mesoscopic description is desirable in the chaotic regime of deterministic dynamics, the macroscopic equations might still keep some sense. Anyway, the properties of the deterministic chaotic attractor are consistent with their microscopic analogues of individual simulation runs.

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